TITLE: Supported Dense Ceramic Membranes for Oxygen Separation

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ABSTRACT

The objective of this project is to explore fundamental and practical issues associated with the fabrication of dense thick-film ceramic membranes on porous ceramic supports. Most of the research has focused on the $SrFeCo_{0.5}O_x$ composition, which has been reported to possess high oxygen permeability as well as stability against chemical reduction. The primary problems that confront fabrication of supported dense ceramic membranes is associated with reliable densification of the membrane layer on a porous substrate without introducing cracks or defects to the membrane layer, densifying the support, or promoting chemical interaction with the support. In this project, we have explored the use of ultrafine aerosol-derived powders to produce the membrane layer, coupled with chemically compatible coarser powders which are used to fabricate a pre-sintered porous support.

In the first two years of this project we determined appropriate conditions for the sintering of porous $SrFeCo_{0.5}O_x$ supports, and initiated studies of the sintering behavior and phase evolution of thick supported $SrFeCo_{0.5}O_x$ films. Porous $SrFeCo_{0.5}O_x$ supports were fabricated by pressing discs (~1 μm thick) from micron-sized commercial $SrFeCo_{0.5}O_x$ powder, followed by sintering in air at 1050 °C. This provided acceptable support strength while retaining relatively high porosity and low gas flow resistance. Fine (0.2-0.4 μm diameter) crystalline $SrFeCo_{0.5}O_x$ powder was produced by aerosol pyrolysis at 700 °C, formed into a paste with polyethylene glycol (18 wt% powder), and deposited as a thick film onto the supports by doctor blading. The supported films were then sintered in air or nitrogen. With air sintering, large plate-shaped grains form which leads to a stable open (porous) structure that is very difficult to densify, short of complete densification of both film and support at sintering temperatures near 1200 ºC. The as-produced aerosol powder consisted mainly of the $Sr(Co,Fe)O_3$ phase, and air sintering produced a nearly single-phase material which is structurally very similar to the $Sr_7Fe_{10}O_{22}$ layered perovskite structure. This corresponds to the structure that has been reported having

high oxygen permeability. Nitrogen sintering leads to rapid densification of the film at temperatures above 1000 ºC. The film shrinkage associated with this sintering led to large scale cracks and, ultimately, isolated dense islands of film on the porous substrate. The film morphology after sintering in nitrogen was relatively smooth with small, roughly equiaxed grains. XRD revealed a mixture of crystalline phases ($Sr_7Fe_{10}O_{22}$-type, perovskite Sr(Co,Fe)O_{3-x}, brownmillerite Sr(Fe,Co)$O_{2.5}$ and CoO). This mixture of phases may be convertible to the desired layered perovskite structure, but this has not yet been demonstrated.

In these investigations, we have not yet successfully prepared dense membrane layers of sufficient quality for oxygen permeation measurements. The fundamental problems preventing defect free membrane fabrication seem to be related to: (1) the inevitable stress associated with constrained sintering of a film, and (2) the high degree of shrinkage needed because of the low solid content of the paste we have used. Our most recent investigations have been oriented toward these problems. A strategy was conceived and tested wherein composite MgO/$SrFeCo_{0.5}O_x$ supports were shown to have inhibited sintering, enabling higher sintering temperatures to be used where significant melting should occur in the film (thus presumably alleviating stress buildup in the film). The composite supported films sintered in air at 1300-1400^{o}C were found to be uniform, with good coverage, and cracking in the film layer was reduced. However films still did not completely densify for reasons that are still not completely clear. We have also been exploring more sophisticated paste formulations and thermal processing profiles to minimize cracking. The new paste formulations incorporate a dispersant (castor oil) and organic solvent system to increase powder loading, and a plasticizer (polyvinyl butyral) to inhibit cracking. Characterization of these films is just beginning, and results will be presented at the annual meeting. Efforts to use counterflow MOCVD as a defect mending technique have also continued in the past year. Though we previously reported that Fe(tmhd)$_3$ in air was a suitable system for depositing iron oxide by this method, we have so far been unsuccessful in localizing the deposition in such a way that the pores and flaws are selectively blocked.

ARTICLES, PRESENTATIONS AND STUDENT SUPPORT

JOURNAL PUBLICATIONS

- none published at this time

CONFERENCE PRESENTATIONS

- T. Ward,* D. Xia, R. Chitthuri, "The Processing and Mending of Dense Thick Film Ceramic Membranes Using Ultrafine Powders", platform presentation, 1999 Annual Meeting of the American Institute of Chemical Engineers, Oct. 31-Nov. 5, 1999, Dallas, TX.
- T.L. Ward,* D. Xia, and R. Chitthuri, "The Use of Aerosol and Vapor Processing in the Fabrication of Dense Mixed-Conducting Ceramic Films", platform presentation, Vapor Phase Synthesis and Materials III, Engineering Foundation Conference, July 18-23, 1999, Helsinki, Finland.
- D. Xia, H. Zhang, and T. L. Ward*, “The Processing of Dense Thick-Film Sr-Co-Fe-O Membranes Using Aerosol-Derived Powders”, accepted as platform presentation, 2001 National Meeting of the North American Membrane Society, May 16-18, 2001, Lexington, KY.

THESES

- D. Xia, “The Fabrication and Sintering of Sr-Co-Fe-O Membrane Supports and Films”, M.S. Thesis, University of New Mexico, December 2000.

STUDENTS SUPPORTED

- Deying Xia (M.S.)
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